RI 8957

Bureau of Mines Report of Investigations/1985

Defluorination of Byproduct Zinc Concentrates

By R. B. Prater, Jr., V. R. Miller, and E. R. Cole, Jr.

UNITED STATES DEPARTMENT OF THE INTERIOR

Defluorination of Byproduct Zinc Concentrates

By R. B. Prater, Jr., V. R. Miller,
and E. R. Cole, Jr.

CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mm	millimeter
g	gram	ppm	part per million
g/L	gram per liter	pct	percent
h	hour	r/min	revolution per minute
min	minute	wt pct	weight percent
mL	milliliter		

DEFLUORINATION OF BYPRODUCT ZINC CONCENTRATES

By R. B. Prater, Jr.,[1] V. R. Miller,[2] and E. R. Cole, Jr.,[3]

ABSTRACT

The Bureau of Mines conducted research to separate the F from byproduct Zn concentrates obtained from fluorspar (CaF_2) production, as part of the Bureau's effort to devise efficient, environmentally acceptable technology for recovering Zn from resources considered undesirable by Zn producers. Sulfuric acid (H_2SO_4) was found to be effective in F removal, while ammonium carbonate [$(NH_4)_2CO_3$] was not. The most important variables for reducing the necessary residence time were found to be temperature and agitation. Optimum leaching conditions were 75° C and 500 r/min for 2 h at 40 pct solids with 0.2 g acid per gram of concentrate, which resulted in a 98.3-pct F extraction. Zinc losses during F removal were in the range of 2 to 3.3 pct. Other elements such as Fe, Cd, Ca, and Cu were also partially dissolved. About 93 pct of the F was removed from the leach solution by neutralization and precipitation with calcium hydroxide [$Ca(OH)_2$]. Additional treatment might be necessary to limit the buildup of soluble elements in the recycled leach solution.

[1]Metallurgist.
[2]Supervisory research physicist.
[3]Research supervisor.
 Rolla Research Center, Bureau of Mines, Rolla, MO.

INTRODUCTION

This work was conducted by the Bureau of Mines to devise efficient, environmentally acceptable technology for recovering Zn from resources considered undesirable by Zn producers.

More than 90 pct of the fluorspar produced in the United States comes from southern Illinois and western Kentucky. During the production of this fluorspar, a sphalerite (ZnS) concentrate is also produced. Since this concentrate is a byproduct, it may contain as much as 1 pct F, which reduces its marketability. Essentially all the Zn produced in this country is now made by the roast-leach-electrowinning (electrolytic) process (1).[4] Electrolytic Zn smelters will not use Zn concentrates containing F for two reasons. First, they do not want the material because of F emissions that would occur during roasting. Second, but perhaps more important, fluorides in the electrolyte will etch the Al cathodes used for depositing Zn and cause the Zn to stick (2-4). This results in loss of Zn and, in some cases, the Al cathode as well. Zinc as a byproduct of fluorspar mining is not a major source of the metal, but the lack of a market for this Zn material adversely affects the economics for the production of fluorspar, a vital and rather scarce commodity. Therefore, the Bureau considered it urgent to find a method to remove or negate the effects of F in these concentrates in order to maintain a healthy and economic fluorspar mining operation in the United States. Overseas markets for the Zn concentrates still exist, but heavy penalties are exacted for F content, and shipping costs are prohibitive.

The problem of F in the Zn concentrates from fluorspar mining is not a new one and prompted work in the late 1930's that led to several patents. The first patent issued (5) utilized H_2SO_4 at ambient temperature, but this was found to be a slow process and not fully effective in removing the F unless prolonged for uneconomic time periods. Later work (6-7) improved the F removal by using H_2SO_4 at elevated temperatures (50° to 90° C) for shorter periods of time while adding Al or B compounds to reduce solubilization of the Zn. These patents were not implemented on an industrial scale because the urgent need for Zn during World War II provided a ready market. In recent times, these patents have not been used because of mineralization changes in ores from the many small mines developed in the ensuing 40 years and the continued availability of the overseas markets. However, with increased shipping costs and the penalties exacted, this overseas market is becoming an uneconomical solution.

In the present research, the decision to try H_2SO_4 to remove the F from recent byproduct Zn concentrates was made in light of the fact that some smelters use an H_2SO_4 preleach to remove Mg from regular Missouri Zn concentrates. If this leach could also remove F, then the byproduct Zn concentrates from fluorspar mining could be processed with the Missouri Zn concentrates. The response of the new concentrates to leaching with H_2SO_4 was first determined in regular leaching experiments, as well as the response to leaching with $(NH_4)_2CO_3$ (8, p. 371). Following this, a leaching experiment was set up to simulate a continuous countercurrent three-stage leach to reduce the acid content and raise the F content of the final leach solution.

MATERIALS

ZINC CONCENTRATES

Samples of Zn concentrate were obtained from the Ozark-Mahoning Co. concentrator

---

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

at Rosiclare, IL, and the Inverness Mining Co. concentrator at Cave In Rock, IL. Chemical analyses of the concentrates are reported in table 1.

The concentrates were tested both as received and after grinding. The as-received samples were dried at 105° C and then screened at 35 mesh. After the

TABLE 1. - Chemical analyses of Zn concentrates, percent

Element	Ozark	Inverness
Zn.....................	60.0	60.2
Fe.....................	1.29	.92
Cd.....................	.72	1.25
Pb.....................	.76	.71
Ca.....................	.36	.78
F......................	.310	.411
Cu....................	.19	.13

agglomerates produced by drying were broken up, the samples were 100 pct minus 35 mesh. The other samples were wet-ground for 30 min in a porcelain jar mill, yielding a product that was 100 pct minus 200 mesh when wet-screened. The ground samples were then filtered, dried at 105° C, and screened at 35 mesh.

REAGENTS

The H_2SO_4 used in the leaching experiments was either reagent grade (95 to 98 pct H_2SO_4) or byproduct "black" acid (92 to 94 pct H_2SO_4) from a Missouri Pb smelter. The $(NH_4)_2CO_3$ used in the leaching experiments and the NaOH used in the gas scrubber were both reagent grade. All solutions were prepared with distilled water.

EQUIPMENT AND PROCEDURE

EQUIPMENT

The concentrates were leached in a 500-mL glass reaction kettle. The kettle was heated with a heating mantle controlled by a variable transformer and a digital temperature controller. The controller, with a resolution of ±1° C, also served to monitor the temperature in the reaction kettle by using a type J thermocouple in a glass thermocouple well.

To minimize liquid loss, the outlet of the reaction kettle was connected to a condenser. Gaseous reaction products such as HF and H_2S were controlled by using an aspirator to pull the gases from the top of the condenser through a trap and into a gas-washing bottle that contained a 1.0N NaOH solution to neutralize and absorb the gases.

Agitation of the leach slurry was performed with a variable-speed motor connected by a flexible shaft to a glass stirring shaft that was fitted with a Teflon[5] fluorocarbon polymer bearing and a single, flat, 76-mm Teflon fluorocarbon polymer stirrer blade.

The typical equipment for a leaching test, as shown in figure 1, also included a timer switch and a temperature indicator to monitor the temperature of the heating mantle.

PROCEDURE

The leaching reagent or reagents were mixed with distilled water, poured into the reactor, and preheated to the desired operating temperature. The concentrate sample was added to the reactor, and the timer was started. At the end of the test, the leach slurry was filtered at the test temperature and the solid residue was washed twice with distilled water at 50° C. The leach solution and the two wash solutions were kept separate, and their volumes were measured at room temperature. The residue was dried at 105° C and weighed.

All of the solid samples and most of the solution samples were analyzed for F, using a fluoride specific ion electrode.[6] Analyses for other elements were done by standard atomic absorption spectrophotometry methods.

[5]Reference to specific products does not imply endorsement by the Bureau of Mines.

[6]The authors thank Marion Dattilo, chemist, and William Corey, Sr., physical science technician, Rolla Research Center, for their assistance in developing the analytical procedures.
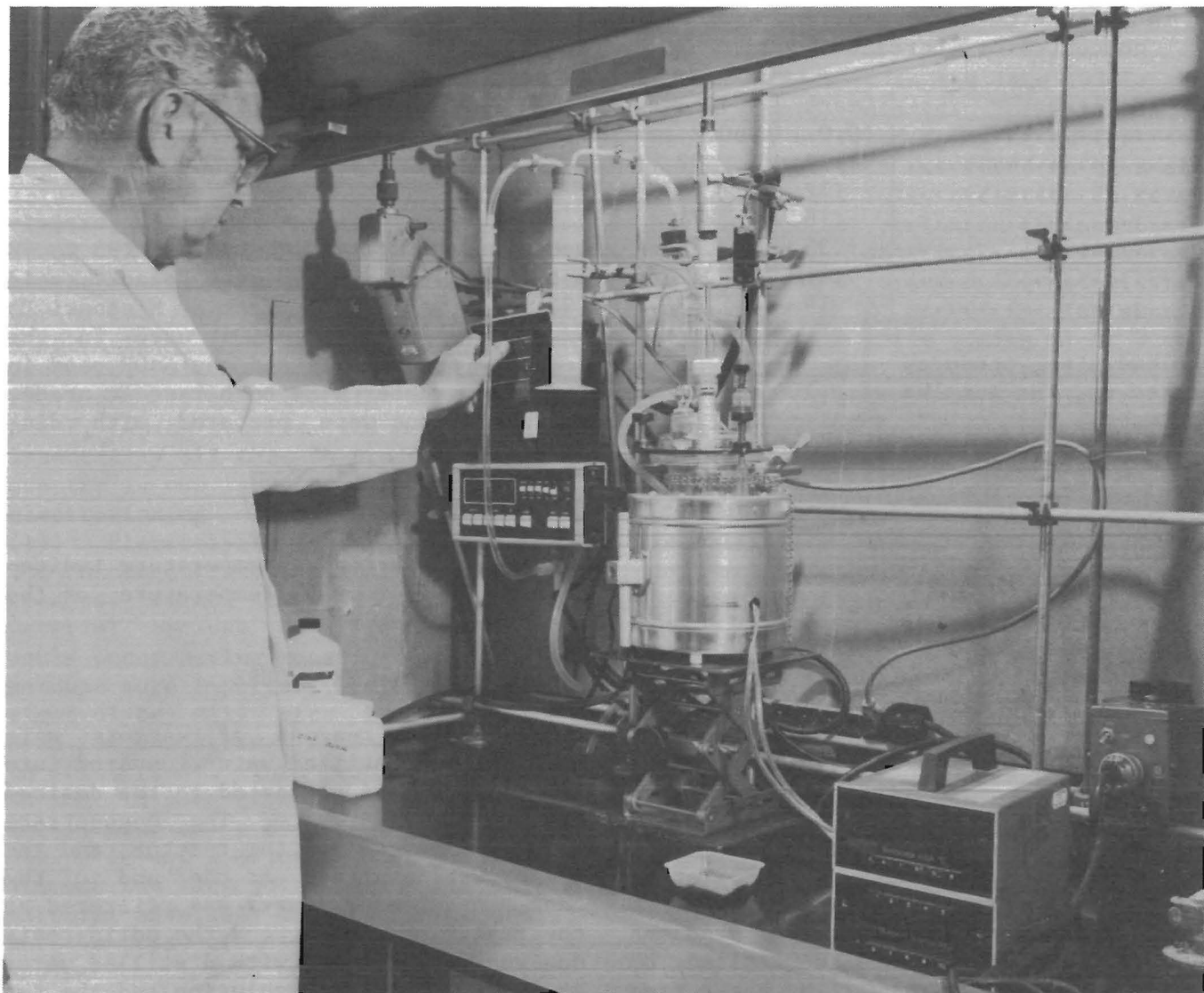
FIGURE 1. - Leach test apparatus.

RESULTS AND DISCUSSION

INITIAL LEACHING TESTS

Each series of leaching tests was set up as a half-fraction of a 2^5 factorial design of resolution V (9, pp. 374-390). However, only in the last series of this type were the tests run in random order, and the time available did not permit the running of a replicate series. The leaching variables and the ranges over which they were examined are listed in table 2.

Leaching With H_2SO_4

The first series of 16 leach tests was designed to give a preliminary indication of the effects of temperature, acid concentration, time, and particle size on the extraction of F. The fifth variable was the origin of the concentrate. The design variables and their test levels are given in table 3.

The F extraction and weight loss results for the first test series are also

TABLE 2. - Leaching variables and test
ranges

Variable	Range
Temperature...............°C..	25-75
Agitation..............r/min..	150-500
Time....................min..	30-240
Solids...............wt pct..	16-40
Particle size..........mesh..	-35 or -200
Reagent[1] concentration..g/L..	20-320
Reagent-to-concentrate ratio.	0.1-0.5

[1]Reagents: $(NH_4)_2CO_3$, H_2SO_4.

given in table 3. All of the tests used
250 mL of diluted acid and 50 g of con-
centrate, resulting in about 16 pct sol-
ids in the reactor.

The residues from the first series of
tests were 2.4 to 7.0 pct lower in weight
than the initial concentrates, and 12.4
to 99.7 pct of the F had been extracted.
There did not appear to be any cor-
relation between weight loss and F
extraction.

In these tests, the "effect" of a vari-
able is the change in the F extraction

caused by going from the low level to the
high level of that variable (9, p. 309).
If the numerical value of the effect is
positive, then the F extraction was in-
creased by going to the high level of
that variable. Interactions between var-
iables occur when their effects are not
additive (9, p. 313). The effects of the
main variables and their interactions
can be calculated by using a table of
contrast coefficients (9, pp. 322-323).
When a half-fraction of a 2^5 design is
used, it is assumed that three-factor and
higher order interactions are negligible
(9, p. 379).

Of the variables tested, only tempera-
ture had a significant effect on increas-
ing F extraction. Increasing the temper-
ature from 25° to 75° C increased the
average F extraction from 34.1 to 78.1
pct. There was an interaction between
acid concentration and particle size. In
the tests at 20 g/L H_2SO_4, reducing the
particle size from 100 pct minus 35 mesh
to 100 pct minus 200 mesh increased the
average F extraction from 39.5 to 59.5
pct. However, in the tests with 100 g/L

TABLE 3. - Effects of temperature, H_2SO_4 concentration, particle size,
and time on F extraction, tests 1 through 16

Temp, °C	H_2SO_4, g/L	Size, mesh	Time, min	Concentrate	Test	F extraction, pct	Weight loss, pct
25...	20	-35	30	Ozark......	1	12.4	4.96
	20	-35	120	Inverness..	5	33.8	3.86
	20	-200	30	...do......	9	23.6	2.48
	20	-200	120	Ozark......	13	42.6	2.42
	100	-35	30	Inverness..	3	18.8	3.04
	100	-35	120	Ozark......	7	47.5	7.04
	100	-200	30	...do......	11	43.8	2.50
	100	-200	120	Inverness..	15	50.0	2.72
75...	20	-35	30	...do......	2	46.9	4.54
	20	-35	120	Ozark......	6	64.8	6.00
	20	-200	30	...do......	10	88.8	3.16
	20	-200	120	Inverness..	14	82.7	3.54
	100	-35	30	Ozark......	4	95.7	5.94
	100	-35	120	Inverness..	8	99.6	5.30
	100	-200	30	...do......	12	46.2	3.02
	100	-200	120	Ozark......	16	99.7	4.08

H_2SO_4, the same particle size reduction reduced the average F extraction from 65.4 to 59.9 pct. There was also an interaction between leaching time and the origin of the concentrate. Increasing the leaching time from 30 to 120 min increased the average F extraction from the Inverness concentrate from 33.9 to 66.5 pct, while the average extractions from the Ozark concentrate were almost constant at 60.2 and 63.7 pct, respectively.

Analyses of the solutions from the leach tests with the highest weight loss and F extraction for 20 g/L acid are given in table 4. In addition to the F, some Zn, Ca, Cd, and Fe were also dissolved. The average total F recovery in the residue, leach solution, and wash water for all 16 tests was 95.6 pct, and the filtrates contained 0.07 to 0.8 g/L F.

Leaching With $(NH_4)_2CO_3$

A similar series of tests was conducted with $(NH_4)_2CO_3$ instead of H_2SO_4 to determine the relative effectiveness of these reagents. The design variables and levels and the test results are listed in

TABLE 4. – Leach solution analyses for tests 6 and 14

	Test 6	Test 14
Composition, g/L:		
Ca.....................	0.561	0.596
Cd.....................	0.028	0.008
Cu.....................	<0.001	<0.001
F.....................	0.417	0.60
Fe.....................	0.226	0.080
Zn.....................	3.02	1.54
Free H_2SO_4............	16.3	18.8
Zn dissolved.......pct..	2.74	1.32

table 5. The residues showed weight losses ranging from 1.2 to 4.5 pct and F extractions of 0 to 13.8 pct.

A comparison of the data from the two sets of leach tests showed the following results for a 2-h leach with 100 g/L reagent:

Reagent	Temp, °C	F extraction, pct
H_2SO_4.......	25	47.5–50
H_2SO_4.......	75	>99
$(NH_4)CO_3$....	50	12.6–13.8

TABLE 5. – Effects of temperature, $(NH_4)_2CO_3$ concentration, particle size, and time on F extraction, tests 17 through 32

Temp, °C	$(NH_4)_2CO_3$, g/L	Size, mesh	Time, min	Concentrate	Test	F extraction, pct	Weight loss, pct
25...	20	-35	30	Ozark......	17	0	3.00
	20	-35	120	Inverness..	21	0	2.18
	20	-200	30	...do......	25	.75	1.22
	20	-200	120	Ozark......	29	7.54	1.28
	100	-35	30	Inverness..	19	5.91	2.70
	100	-35	120	Ozark......	23	0	4.40
	100	-200	30	...do......	27	8.01	2.08
	100	-200	120	Inverness..	31	7.72	2.18
50...	20	-35	30	...do......	18	3.06	1.90
	20	-35	120	Ozark......	22	.95	2.08
	20	-200	30	...do......	26	7.75	1.20
	20	-200	120	Inverness..	30	3.03	1.40
	100	-35	30	Ozark......	20	3.69	4.52
	100	-35	120	Inverness..	24	12.6	2.50
	100	-200	30	...do......	28	9.52	2.38
	100	-200	120	Ozark......	32	13.8	2.60

The work on $(NH_4)_2CO_3$ leaching was therefore discontinued and all subsequent testing was done with H_2SO_4.

Effect of Percent Solids

The particle size of the concentrate was replaced with percent solids in the design for the third series of tests. The design variables and levels and the test results are given in table 6. All of the tests used 250-mL volumes of dilute acid and 100 pct minus 35-mesh concentrate. The solids content of the reaction slurries was varied by using 50 or 175 g of concentrate. The residues had weight losses ranging from 3.5 to 9.5 pct. The tests at 16 pct solids resulted in F extractions of 64.8 to 99.5 pct, while those at 40 pct solids had F extractions of 43.6 to 86.3 pct. Temperature was the only variable with a significant positive effect on F extraction; increasing the temperature from 50° to 75° C increased the average F extraction from 66.2 to 89.0 pct. Percent solids was the only variable with a significant negative effect; raising the solids

content of the leach slurry from 16 to 40 pct reduced the average F extraction from 89.3 to 65.9 pct. There were no significant interactions.

The filtrates from these tests contained 0.46 to 2.25 g/L F. The average F recovery for this test series was approximately 100 pct. Analyses of four of the filtrates are given in table 7, and analyses of two of the corresponding residues are given in table 8. The filtrate analyses indicate that the more aggressive leaching conditions used in this test series resulted in the extraction of some of the Cu from the Ozark concentrate. The other coextracted elements found in the filtrates from the first test series (see table 4) were also present, but at higher concentration levels.

Effect of Agitation

In the third test series, the average F extractions were 80.0 pct for the Ozark concentrate and 75.2 pct for the Inverness concentrate. All of the tests in the fourth series of factorial design leach tests were conducted on 100 pct

TABLE 6. – Effects of temperature, H_2SO_4 concentration, percent solids, and time on F extraction, tests 33 through 48

Temp, °C	H_2SO_4, g/L	Solids, wt pct	Time, min	Concentrate	Test	F extraction, pct	Weight loss, pct
50...	75	16	60	Inverness..	33	64.8	5.94
	75	16	120	Ozark......	37	86.0	7.86
	75	40	60	...do......	35	43.6	6.98
	75	40	120	Inverness..	39	49.8	3.54
	100	16	60	Ozark......	34	82.5	8.08
	100	16	120	Inverness..	38	85.2	5.30
	100	40	60	...do......	36	52.9	3.77
	100	40	120	Ozark......	40	64.8	6.84
75...	75	16	60	...do......	41	98.0	8.54
	75	16	120	Inverness..	45	99.5	6.22
	75	40	60	...do......	43	65.8	4.38
	75	40	120	Ozark......	47	79.5	7.74
	100	16	60	Inverness..	42	99.1	5.98
	100	16	120	Ozark......	46	99.2	9.52
	100	40	60	...do......	44	86.3	7.59
	100	40	120	Inverness..	48	84.8	3.71

TABLE 7. – Leach solution analyses
for tests 45 through 48

	Test 45	Test 46	Test 47	Test 48
Composition, g/L:				
Ca.....................	0.70	0.71	0.38	0.38
Cd.....................	0.04	0.04	0.15	0.09
Cu.....................	<0.001	0.037	0.119	<0.001
F......................	0.80	0.56	1.54	2.25
Fe.....................	0.098	0.208	0.714	0.302
Zn.....................	2.57	3.55	12.4	7.25
Free H_2SO_4.............	65.3	87.0	46.5	62.3
Zn dissolved.......pct..	2.26	3.20	3.32	1.96

minus 35-mesh Inverness concentrate because of its somewhat greater resistance to F extraction. The design variables and their test levels are given in table 9. The weight ratio of acid to concentrate was used rather than acid concentration, and agitation was added as a new variable. All of the tests used 250 mL of dilute acid; but four different acid concentrations, ranging from 52 to 320 g/L, and four different concentrate weights, ranging from 64.5 to 198.7 g, were used to obtain the appropriate weight ratio and percent solids. The tests in this series were run in random order rather than in standard order (9, p. 323) as in the first three test series.

TABLE 8. – Leach residue analyses
for tests 45 and 46, percent

Composition	Test 45	Test 46
Ca.....................	0.25	0.22
Cd.....................	1.31	.45
Cu.....................	.13	.16
F......................	.0021	.0027
Fe.....................	.88	.69
Zn.....................	60.2	62.1

TABLE 9. – Effects of temperature, agitation rate, percent solids, acid-to-concentrate ratio, and time on F extraction, tests 49 through 64

| Temp, °C	Agitation, r/min	Solids, wt pct	H_2SO_4-to-conc ratio	Time, min	Test	F extraction, pct	Weight loss, pct
50...	150	20	0.2	240	63	65.4	5.21
	150	20	.4	120	50	74.8	4.88
	150	40	.2	120	58	62.0	3.08
	150	40	.4	240	61	47.4	3.05
	500	20	.2	120	56	58.1	5.35
	500	20	.4	240	57	92.4	4.92
	500	40	.2	240	49	92.3	4.26
	500	40	.4	120	52	96.4	2.37
75...	150	20	.2	120	64	84.2	5.85
	150	20	.4	240	60	99.7	6.56
	150	40	.2	240	54	89.0	3.74
	150	40	.4	120	62	78.4	4.46
	500	20	.2	240	51	96.6	5.44
	500	20	.4	120	53	99.7	6.02
	500	40	.2	120	59	98.3	3.69
	500	40	.4	240	55	98.0	3.61

The F extraction and weight loss results of the fourth test series are also given in table 9. The residues had weight losses of 2.4 to 6.6 pct. Fluorine extractions of 58.1 to 99.7 pct were achieved in the tests at 20 pct solids, and 47.4 to 98.3 pct at 40 pct solids. Temperature was the only variable with a significant effect and no interactions. Increasing the temperature from 50° to 75° C increased the average F extraction from 73.6 to 93.0 pct. There was an interaction between the acid-to-concentrate ratio and percent solids. In the tests at 20 pct solids, increasing the acid-to-concentrate ratio from 0.2 to 0.4 increased the average F extraction from 76.1 to 91.6 pct; but at 40 pct solids, the extractions decreased from 85.4 to 80.1 pct when the ratio was increased. There was also an interaction between percent solids and agitation rate. The increase in agitation from 150 to 500 r/min increased the average F extraction from 81.0 to 86.7 pct in the tests at 20 pct solids. However, the same increase in agitation in the tests at 40 pct solids resulted in a much larger change in the average F extraction, from 69.2 to 96.3 pct.

The filtrates from these tests contained 0.58 to 2.88 g/L F. The average total F recovery for this test series approached 100 pct. The F content of the unleached concentrate samples ranged from 0.26 to 0.82 g. The caustic scrubber solutions from eight of these tests were analyzed and found to contain 0.04 to 2.6 ppm F, with an average of 0.75 ppm. The 2.6-ppm figure represents 0.0087 pct of the F in the head sample for that particular test. The very low levels of F in the scrubber solution and the high recoveries in the leach solutions and residues both indicate that any F losses in the vapor phase were minimal.

COST REDUCTION TESTS

In actual practice, to minimize cost, the leaching would probably be done with byproduct or waste acid, such as the "black" acid produced at the Pb smelters in Missouri. It would also be desirable to reduce the amount of Zn that is

dissolved. According to Abbott [5], the HF that is formed when the H_2SO_4 dissolves the fluorspar according to reaction A may react with the sphalerite according to reaction B.

$$H_2SO_4 + CaF_2 \rightarrow CaSO_4 + 2HF. \quad (A)$$

$$2HF + ZnS \rightarrow ZnF_2 + H_2S. \quad (B)$$
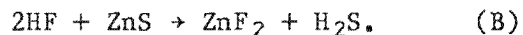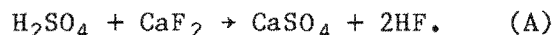
Since some H_2S was apparently evolved during the leach tests, this reaction may have been taking place. According to Anderson [6], the addition of soluble Al compounds to the leach may form AlF_3 in solution and thus reduce the amount of Zn lost as soluble ZnF_2.

A series of six leaching tests was conducted to determine the effects of using "black" acid and aluminum sulfate $[Al_2(SO_4)_3]$. All of the tests were performed at 40 pct solids, 0.2 g acid per gram of concentrate, 75° C, 500 r/min agitation, and 2 h duration. The two grades of acid were both diluted to 145.3 g/L, and the amount of $Al_2(SO_4)_3$ that was used was approximately 150 pct of the stoichiometric requirement to form AlF_3 with the F in the concentrate sample. The test conditions and results are given in table 10. With only one exception (test 68), the change in reagents had no effect on the weight loss. The change in reagents improved the F extractions slightly; but within the limits of experimental error, the addition of $Al_2(SO_4)_3$ to the leach had no effect on the Zn dissolution. Both the presence of H_2S and the partial dissolution of the Zn, therefore, can probably be attributed to reaction C [10, p. 46].

$$H_2SO_4 + ZnS \rightarrow ZnSO_4 + H_2S. \quad (C)$$
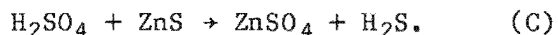
SIMULATED COUNTERCURRENT TESTS

Although the F can be extracted from the concentrates by using acid-to-concentrate ratios, temperatures, and residence times similar to those used to remove Mg from Missouri Zn concentrates, the Mg preleach is operated cocurrently, and the resulting low acid concentration may cause the F to precipitate. An effective process for the removal of F from these

TABLE 10. – Effects of "black" acid and $Al_2(SO_4)_3$ on F extraction,
tests 65 through 70

Test	Concentrate	Acid	$Al_2(SO_4)_3$	Weight loss, pct	F extraction, pct	Zn dissolved, pct
65	Ozark......	Reagent...	No	7.44	96.7	3.02
66	Inverness..	...do.....	No	4.03	98.5	2.14
67	Ozark......	...do.....	Yes	7.46	97.3	3.21
68	Inverness..	...do.....	Yes	3.89	99.5	2.12
69	Ozark......	"Black"...	Yes	7.48	97.7	NA
70	Inverness..	...do.....	Yes	4.08	99.5	NA

NA Not analyzed.

concentrates would consist of a countercurrent leach with solution recycle and acid makeup. This would maximize the levels of F and other elements dissolved from the concentrates and minimize the acid level of the solution that would be bled off for treatment prior to recycle to the process.

A series of leach tests was set up to simulate a continuous countercurrent three-stage leach. The flowsheet for the tests, shown in figure 2, is derived from one described by Treybal (11, p. 15-15) for liquid extraction testing. The 15

tests, conducted over a 5-day period, all used the same conditions: 1 h at 75° C and 500 r/min. Each addition of fresh concentrate was 178 g of a 1:1 mixture of minus 35-mesh Ozark and Inverness concentrates (40 pct solids in the slurry), and each addition of "fresh" acid was 250 mL of a composite leach solution (CLS 9/9-1) from previous tests, resulting in a ratio of 0.153 g acid to 1 g of concentrate.

Under equilibrium conditions, the batches of concentrate and acid solution would be reacted three times in a countercurrent flow. With only 15 tests in
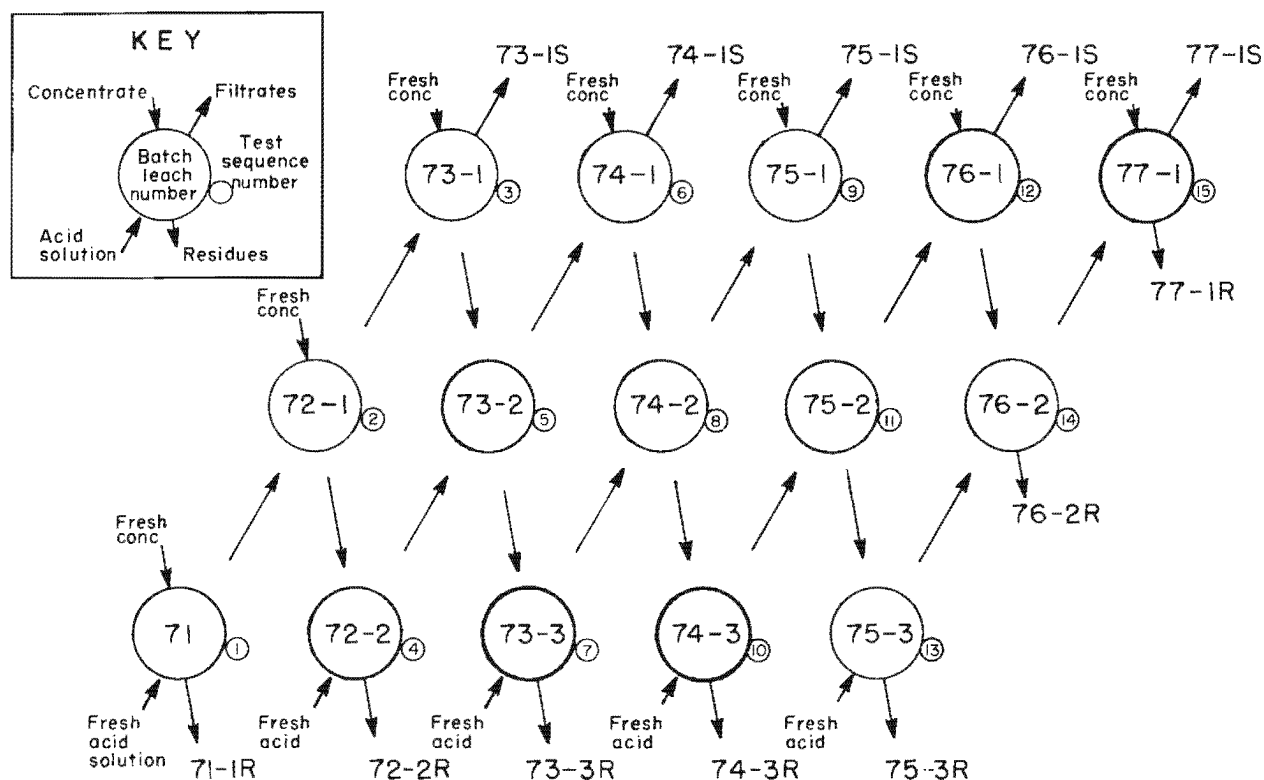

FIGURE 2. – Flowsheet of batch simulation of continuous countercurrent three-stage leach.

the flowsheet, the filtrate designated 77-1S and the residue designated 75-3R are the only samples that approach their equilibrium values. Additional tests would have been required to confirm that there were no additional changes in the assay values. The intermediate filtrates were saved at room temperature, and the intermediate, unwashed residues were sealed in plastic bags until used in the appropriate subsequent test according to the flowsheet. Water was added, as necessary, to complete the transfer of the residues to the reactor and to maintain filtrate volumes near 250 mL. The final residues were washed with 250 mL of a composite second wash solution from previous tests, followed by a second wash of 250 mL of warm water. The first washes from all tests were combined, as were the second washes.

The assays of the "fresh" acid (composite leach solution CLS 9/9-1) and final leach filtrate 77-1S are given in table 11. As expected, three stages of leaching reduced the acid content and raised the concentration of the soluble species. The Ca assay is constant because the excess precipitates out as gypsum at 25° C.

The composite wash water used for the first residue wash contained 49.4 ppm F, while the composite first wash and the composite second wash from the 15 tests contained 0.32 g/L and 46.5 ppm F, respectively. The first four filtrates in the series (73-1S through 76-1S) contained 2.26, 4.24, 4.56, and 4.20 g/L F, respectively.

In previous single-leach tests, the calculation of percent F extraction was based on the head assay and weight and the residue assay and weight. In these tests, the additional handling of the residues could have resulted in additional sample losses, so a linear regression analysis was run on previous data for F extraction as a function of residue assay for both concentrates. Since the concentrates exhibit different weight loss behavior, combining the data results in a lower coefficient of determination (r^2 = 0.97) than when the data for each concentrate are analyzed separately (r^2 = 1.00 in both cases). The F assays of the residue samples and the F extractions calculated by both regression analysis and by weight loss are given in table 12.

TABLE 11. - Compositions of initial and final solutions from simulated
countercurrent three-stage leach, grams per liter

Composition	CLS 9/9-1[1]	77-1S	Composition	CLS 9/9-1[1]	77-1S
Ca.....................	0.28	0.28	Fe.....................	0.24	0.76
Cd.....................	.07	.26	Mg.....................	.09	.28
Cu.....................	.011	.073	Zn.....................	6.14	18.5
F.....................	1.58	3.95	Free H_2SO_4...........	109.1	60.0

[1]Composite leach solution from previous tests, used as feed acid.

TABLE 12. - Residue F assays and extractions
from simulated countercurrent tests

Sample[1]	F, pct	Total weight loss, pct	F extraction, pct	
			By regression	By weight loss
71-1R	0.125	5.22	66.4	67.1
72-2R	.045	7.88	87.8	88.5
73-3R	.017	7.61	95.3	95.6
74-3R	.012	7.59	96.6	96.9
75-3R	.0087	7.63	97.5	97.7
76-2R	.042	6.09	88.6	89.1
77-1R	.220	4.94	40.9	42.0

[1]1R, 2R, and 3R indicate 1, 2, or 3 stages of extraction, respectively (fig. 2).

The extraction results of this series of tests indicate that countercurrent leaching of the byproduct Zn concentrates with H_2SO_4 is a viable technique for reducing the F content of these concentrates. Additional testing would be necessary to optimize the process parameters.

LEACH SOLUTION TREATMENT

A few preliminary tests on treating the leach solution to remove the F were conducted. The best results were obtained when a solution containing 19 g/L H_2SO_4 and 0.57 g/L F was neutralized with $Ca(OH)_2$ and then filtered. About 93 pct of the F was removed, resulting in a solution that contained 39.1 ppm F. This solution could be used to dilute fresh acid for leaching, but additional treatment to remove the remaining F and other solubilized elements would be necessary before it could be discharged to the environment. The type of leaching process and its operating conditions would determine the amount of F and other elements dissolved and their concentration in the leaching solution. The need for a bleed stream and the type of treatment needed would be determined by the effect of the dissolved elements on the F extractions.

CONCLUSIONS

In the H_2SO_4 leaching of Zn concentrates for F removal, the most important variables for reducing the necessary residence time are temperature and agitation. The optimum batch leaching conditions at 75° C and 500 r/min were 2 h at 40 pct solids and 0.2 g acid per gram of concentrate, resulting in an F extraction of 98.3 pct.

Zinc losses to the leach solution were in the range of 2.0 to 3.3 pct. A number of other elements in the concentrates, including Fe, Cd, Ca, and Cu, were also partially dissolved, resulting in a solution that might require a bleed stream for partial purification before recycling to the leach.

Batch or countercurrent H_2SO_4 acid leaching is an effective method of removing F from these byproduct concentrates, but its application or the selection of the leaching method and operating conditions to be applied would depend heavily on the marketing conditions and economics of the process. Variables that would need to be considered include the degree of F extraction required, the level of Zn dissolution allowed, and the availability of processes to recover or safely dispose of the elements contained in the leach solution.

REFERENCES

1. Cammarota, V. A., Jr. Zinc. Ch. in BuMines Minerals Yearbook 1980, v. 1, pp. 883-912.

2. Kammel, R., and H. Saadat. (Adherence of Electrolytic Zinc to Aluminum Cathodes.) Metall (Berlin), v. 30, No. 6, 1976, pp. 551-555; Chem. Abstr., v. 85, 1976, No. 69964.

3. Kelley, F. H. C. Adherence of Electrodeposited Zinc to Aluminum Cathodes. J. Electrochem. Soc., v. 101, May 1954, pp. 239-243.

4. Klimenko, V. L. (Causes of the "Difficult Stripping" of Cathodically Deposited Zinc.) Tsvetn. Met., v. 29, No. 9, 1956, pp. 35-43; Chem. Abstr., v. 51, 1957, No. 12702.

5. Abbott, F. C., S. R. B. Cooke, and C. O. Anderson. Method of Removing Fluorspar From Zinc Concentrates. U.S. Pat. 2,137,600, Nov. 22, 1938.

6. Anderson, C. O., R. J. Stengl, and F. C. Abbott. Method of Purifying Zinc Concentrates. U.S. Pat. 2,291,520, July 28, 1942.

7. _____. Method of Purifying Zinc Concentrates. U.S. Pat. 2,291,521, July 28, 1942.

8. Partington, J. R. General and Inorganic Chemistry. St. Martin's Press, 4th ed., 1966, 926 pp.

9. Box, G. E. P., W. G. Hunter, and J. S. Hunter. Statistics for Experimenters. Wiley, 1978, 653 pp.

10. Romankiw, L. T., and P. L. DeBruyn. Kinetics of Dissolution of Zinc Sulfide in Aqueous Sulfuric Acid. Ch. in Unit Processes in Hydrometallurgy, ed. by M. E. Wadsworth and F. T. David. Gordon and Breach, 1964, pp. 45-65.

11. Treybal, R. E. Liquid Extraction. Sec. in Chemical Engineer's Handbook, ed. by R. H. Perry and C. H. Chilton. McGraw-Hill, 5th ed., 1973, pp. 15-1 to 15-24.